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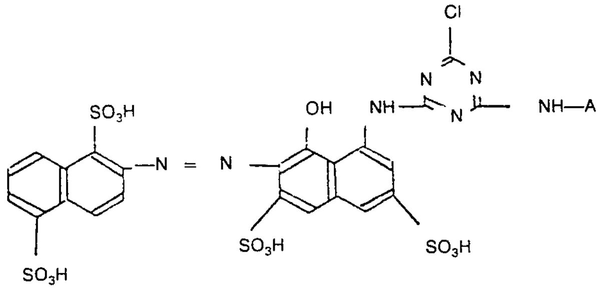
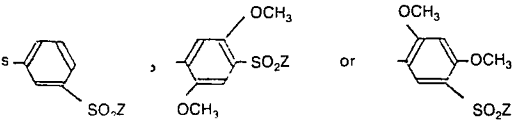
(54) **Reactive monoazo dyes, a process for their production and their use for dyeing cellulosic fibers and cellulosic textiles.**

(57) Reactive monoazo dyes of the general formula (I)



wherein A is



in which Z is $-CH_2CH_2OSO_3H$ or $-CH=CH_2$, and process for their preparation. These dyes are useful for dyeing cellulose fibers in brilliant red colors with good fastnesses, particularly to chlorine, light and perspiration light, as well as good levelling properties.

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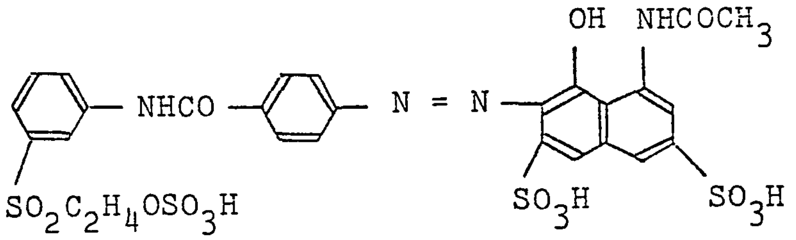
Our Ref.: P 713 EP Case: A4749-02
SUMITOMO CHEMICAL COMPANY, LIMITED, Osaka / Japan
Priority: July 13, 1979, Japan, No. 89650/79

"Reactive Monoazo Dyes, a Process for their Production and their Use for Dyeing Cellulosic Fibers and Cellulosic Textiles"

The present invention relates to novel reactive monoazo dyes and their salts, including alkali metal salts, for dyeing cellulosic textile goods such as filaments, fibers, yarns and textiles in brilliant red colors.

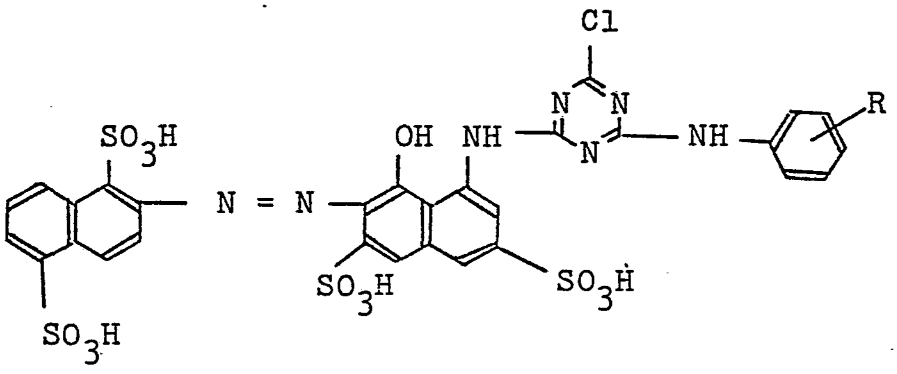
It is well known that dyes having a β-sulfatoethylsulfone group, or so-called vinylsulfone type reactive dyes, are used for dyeing fiber materials. Generally, however, materials dyed with azo red reactive dyes of this kind are not brilliant in shade, and besides they are insufficient in chlorine fastness so that there is often caused a problem of discoloration due to chlorine in **tapwater.** For example, a dye of this kind having the following formula (a) is known, as disclosed in USP 3,008,950,



(a)

This dye is, however, not satisfactory in chlorine fastness (1st grade, ISO method).

There are also known reactive red dyes having a monochlorotriazinyl group. Generally, however, these reactive dyes require high dyeing temperatures and are unsuitable for exhaustion dyeing, so that they cannot produce the desired color density when used for dip dyeing. Accordingly they are only used for printing. Besides, these dyes produce dyed materials of insufficient acid stability. Thus the dyes of this kind are not always satisfactory in practical use. For example, a monochlorotriazinyl reactive dye of the following formula (b) is disclosed in British Pat. 899,376,

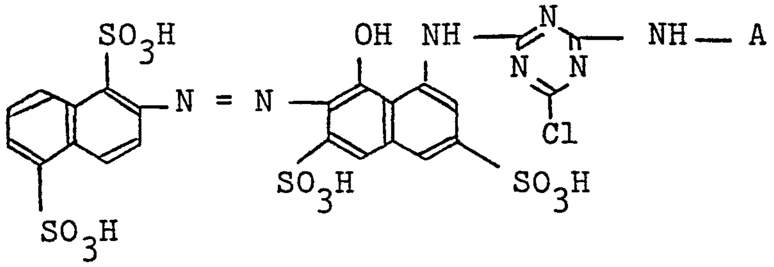


(b)

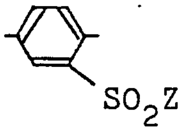
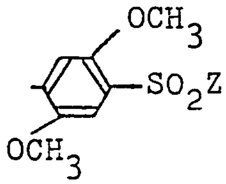
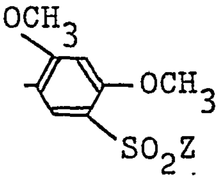
wherein R is a hydrogen or halogen atom or a sulfonic acid or methyl group. However, the acid stability of materials dyed with this dye is insufficient (approximately 3rd grade).

For the reasons described above, the inventors made extensive studies to find a red reactive monoazo dye having particularly superior chlorine fastness, high acid stability, superior suitability for exhaustion dyeing and giving a brilliant red color. As a result, it was found that a reactive dye having both a β-sulfatoethylsulfonyl group and a monochlorotriazinyl group as reactive groups can produce red dyeings meeting these requirements.

The present invention thus provides reactive monoazo dyes of the general formula (I),



(I)

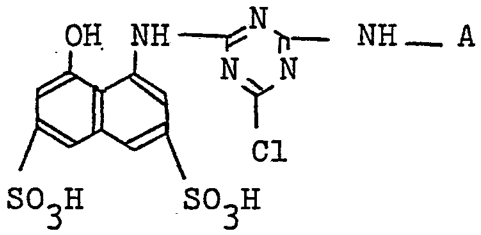
wherein A is  ,  or 

in which Z is $-CH_2CH_2OSO_3H$ or $-CH=CH_2$, and a process for producing the compound of the general formula (I), which comprises,

(i) reacting cyanuric chloride with 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid or an aniline compound of the formula (II),

$$A - NH_2 \qquad (II)$$

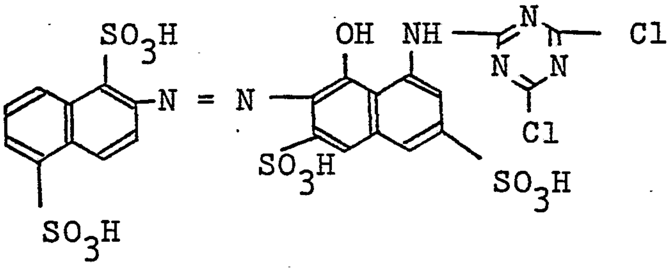
wherein A is as defined above, followed by reaction with the aniline compound (II) or 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid, respectively, to obtain a monochlorotriazinyl compound of the formula (III),



(III)

wherein A is as defined above, and reacting the monochlorotriazinyl compound (III) with diazotized 2-amino-1,5-naphthalenedisulfonic acid,

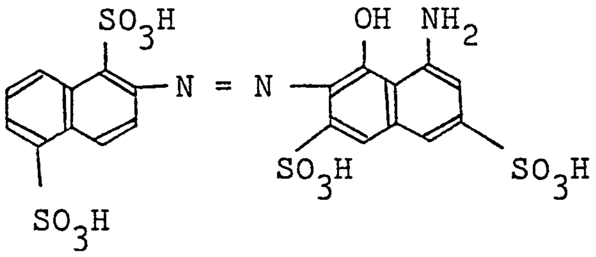
(ii) reacting 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid with cyanuric chloride and thereafter with diazotized 2-amino-1,5-naphthalenedisulfonic acid tc obtain a dichlorotriazinyl compound of the formula (IV),



(IV)

and reacting the dichlorotriazinyl compound (IV) with the aniline compound of the formula (II),

(iii) reacting 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid with a diazotized 2-amino-1,5-naphthalenedisulfonic acid under alkaline conditions to obtain a monoazo compound of the formula (V),

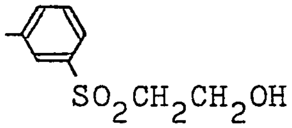


(V)

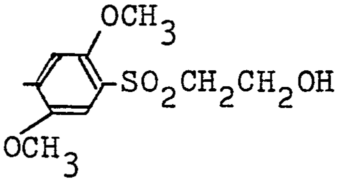
and reacting the monoazo compound (V) with cyanuric chloride and the aniline compound of the formula (II) in this order, or

(iv) carrying out a reaction in a manner (i), (ii) or (iii) as defined above, except using an aniline compound of the formula (VI) in place of the aniline compound of the formula (II), the formula (VI) being

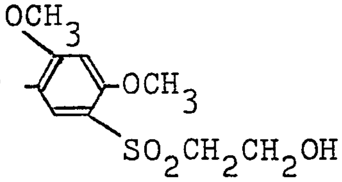
B-NH$_2$, wherein B is



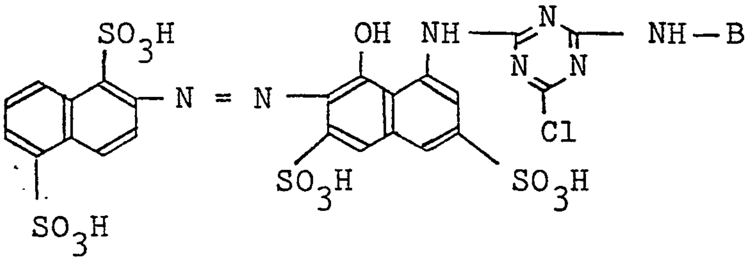
,



or



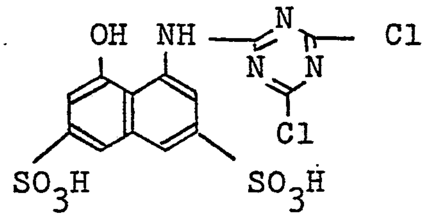
, and reacting the resulting compound of the formula (VII),



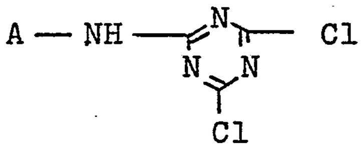
(VII)

wherein B is as defined above, with sulfuric acid to obtain the compound of the formula (I) having β-sulfatoethylsulfonyl group ($-SO_2CH_2CH_2OSO_3H$) as Z, and if necessary followed by elimination of sulfuric acid to obtain the compound of the general formula (I) having vinyl group ($-CH=CH_2$) as Z.

The first condensation between cyanuric chloride and 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid, the aniline compound of the formula (II) or the monoazo compound of the formula (V) can be carried out at a temperature of 0° - 30°C for 1 - 10 hours under stirring in an aqueous medium preferably containing a surfactant while controlling the pH at 1 - 7 by using an acid binding agent (e.g. sodium hydroxide, sodium carbonate, sodium hydrogen carbonate or potassium carbonate). The second condensation between the obtained dichlorotriazinyl compound of the formula (VIII) or the formula (IX) and the aniline compound of the formula (II) or 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid, respectively,



(VIII)



(IX)

wherein A is as defined above, or between the obtained compound of formula (IV) derived from the first condensation and the anilino compound of the formula (II), can be carried out at a temperature of 5° to 60°C for 1 - 10 hours under stirring while controlling the pH at 3 - 7 by using the same acid-binding agent as described above.

The coupling reaction of the monochlorotriazinyl compound of the formula (III) with diazotized 2-amino-1,5-naphthalenedisulfonic acid can be carried out at a temperature of 0° - 30°C for 1 - 10 hours under stirring while controlling the pH at 4 - 7 by using the same acid-binding agent as described above. The coupling reaction of the compound of formula (VIII) derived from the first condensation between cyanuric chloride and 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid with diazotized 2-amino-1,5-naphthalenedisulfonic acid can be carried out at a temperature of 0 - 20°C for 1 - 10 hours under stirring while controlling the pH at 4 - 7 by using the same acid-binding agent as described above.

In a case where the reaction is carried out using the aniline compound of the formula (VI) in place of the aniline compound of the formula (II), the resulting compound is isolated by salting out, dried, and then esterified in excess amount of esterification agent such as sulfuric acid and/or sulfur trioxide at -5° - 50°C.

The thus obtained dyes of the general formula (I) have a structure such that a monochlorotriazinyl group is located, as a crosslinking group, between a ß-sulfatoethylsulfonyl group which is a reactive group and a parent dye, and therefore the present dye can produce brilliant red dyeings which have never been obtained by conventional vinylsulfone type reactive dyes.

Further, the present dyes of the general formula (I) have disulfonaphthylamine as a diazo component and therefore are remarkably high in absorbance as compared with dyes obtained using other diazo components such as substituted aniline derivatives, and have dyeing characteristics most suitable for dyeing cellulosic fibers and textiles because of the effect of two sulfonic acid groups.

The present dyes of the general formula (I) can be used for dyeing cellulose fiber materials in brilliant red colors by conventional dyeing methods such as exhaustion dyeing, printing and cold batch up dyeing. The cellulose fiber materials to be dyed in accordance with the present invention may, for example, include natural or regenerated cellulosic fibers such as cotton, flax, viscose rayon, viscose and staple fibers, and the like.

The exhaustion dyeing can be carried out at relatively low temperatures in the presence of an acid-binding agent (e.g. sodium carbonate, trisodium phosphate, sodium hydroxide) using a dyeing bath containing sodium sulfate or sodium chloride.

Further the dyes of this invention are capable of level dyeing, can be applied at a wide range of dyeing temperatures and are only minimally affected by the amount of inorganic salt used and bath ratio; hence the dyes have good color reproducibility. Moreover, when the printing process is used, the dyes of the present invention are applied to fibers or textiles together with a thickening agent (e.g. sodium alginate, starch ether) or emulsified product of the agent, an alkali agent (e.g. sodium carbonate, sodium hydrogen carbonate, sodium hydroxide, trisodium phosphate, sodium trichloroacetate, corresponding potassium or alkaline earth metal compounds) or alkali-releasing agent, and if necessary a conventional printing aid (e.g. urea) or dispersing agent, followed by drying and heat treatment particularly in the presence of steam.

The dyes of the present invention give a dyed product with superior properties particularly as regards chlorine fastness (4th grade, ISO method), light fastness and persprirationlight fastness to conventional azo red reactive dyes having a ß-sulfatoethylsulfone group. Particularly, considering that the use of chlorine bleaching agent has recently become popular in washing at home, the dyes of the present invention having a superior chlorine fastness are of high value. Further, the present dyes of superior light fastness and perspiration-light fastness are suitable for dyeing outdoor wear such as sportswear. Also, the dyes of the present invention have a high exhaustion and fixing percentage in exhaustion dyeing, so that dyeings of deep color depths can be obtained.

The dyes are further distinguished by their excellent wash-off properties, easy removability of unfixed dye and very limited dye being left in the dye bath, which also indicates an advantage of the dyes of this invention in respect of waste water treatment.

Moreover, they are distinguished by their good acid stability (4th or 4th to 5th grade).

The conventional reactive dyes with mono- or dichlorotriazinyl groups entailed the problem that the textile materials dyed therewith would be attacked by acidic gases or other substances in the air and decreased in color fastness with the passage of time, but the dyes of this invention have also eliminated problems such as these.

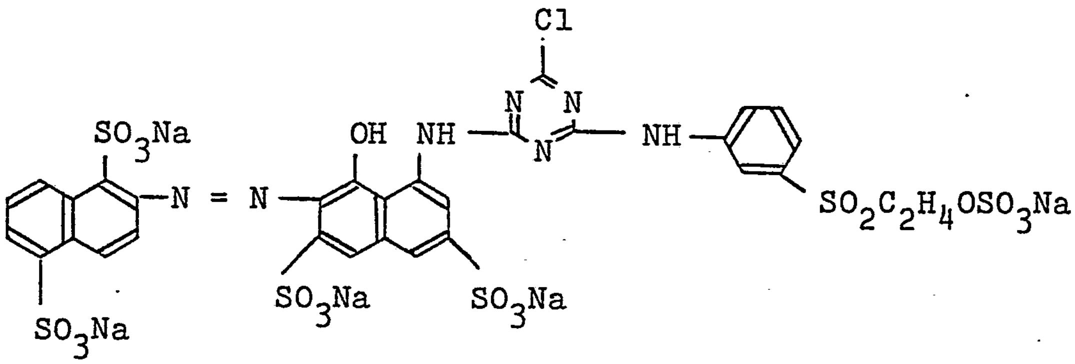
The present invention will be illustrated with reference to the following examples, in which all parts are by weight, and the acid stability was tested as follows: A dyed cloth is dipped in a 1 % acetic acid for 30 minutes and treated at 37 ± 2°C for 6 hours at a pressure of 125 g/cm^2 using a perspirometer.

Example 1

9.2 parts of cyanuric chloride were suspended in ice water, and an aqueous neutral solution containing 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid (15.9 parts) was added thereto. The mixture was cooled and stirred for 5 hours, keeping the pH at 5 or less with a 20 % aqueous sodium carbonate solution if necessary. Thereafter, the mixture was heated to 20°C, and after adding 3-aminophenyl-β-sulfatoethylsulfone (15 parts) it was heated to 30°C while adjusting the pH to 5 or less with a 20 % aqueous sodium carbonate solution, followed by stirring at the same temperature for 5 hours. The reaction solution was then cooled to 10°C or less.

Separately from this, an aqueous suspension (150 parts) containing 2-amino-1,5-naphthalenedisulfonic acid (15 parts) and hydrochloric acid (10 parts) was cooled to 10°C or less, and a solution of sodium nitrite (3.5 parts) in water (10 parts) was added thereto. After stirring the mixture at the same temperature for 3 hours, an excess of the nitrite was removed to obtain a diazo liquor.

This diazo liquor was added to the foregoing reaction solution, and the mixture was stirred for 5 hours at 10°C or less, while adjusting the pH to 6 to 7 with a 20 % aqueous sodium carbonate solution.
After heating to 30°C, the reaction solution was salted out with sodium chloride (150 parts). The precipitated product was filtered, washed and dried at 60°C to obtain 60 parts of a dye having the following formula.



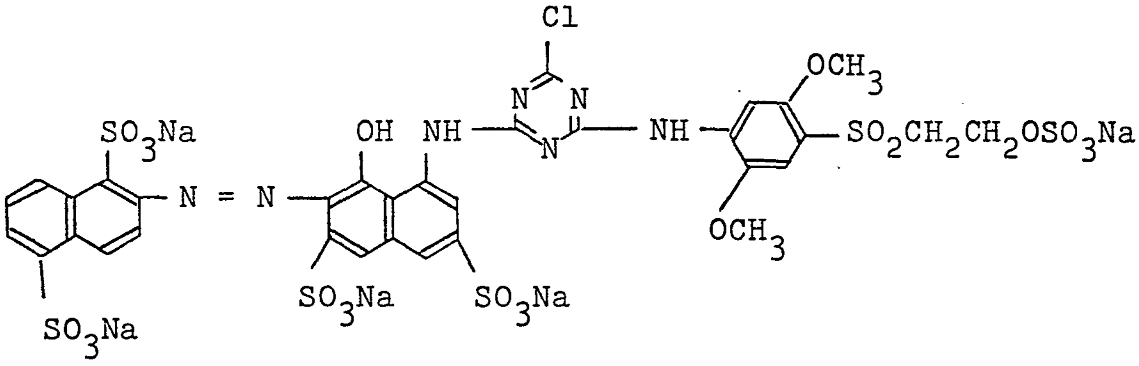
[λ_{max} = 540 nm (measured in a water medium); λ_{max} was measured in the same condition hereinafter]

Example 2

Into an iced aqueous suspension containing cyanuric chloride (9.2 parts) was added a neutralized aqueous solution containing 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid, and the mixture was stirred under cooling for 5 hours while keeping the pH at 3 or less by the addition of a 15 % aqueous solution of sodium hydroxide.

Next an aqueous suspension (150 parts) containing 2-amino-1,5-naphthalenedisulfonic acid (15 parts) and hydrochloric acid (10 parts) was cooled to 10°C or below, and then added to an aqueous solution of sodium nitrite (3.5 parts) in water (10 parts), and the mixture was stirred for 3 hours at the same temperature. Thereafter, excess nitrous acid was decomposed.

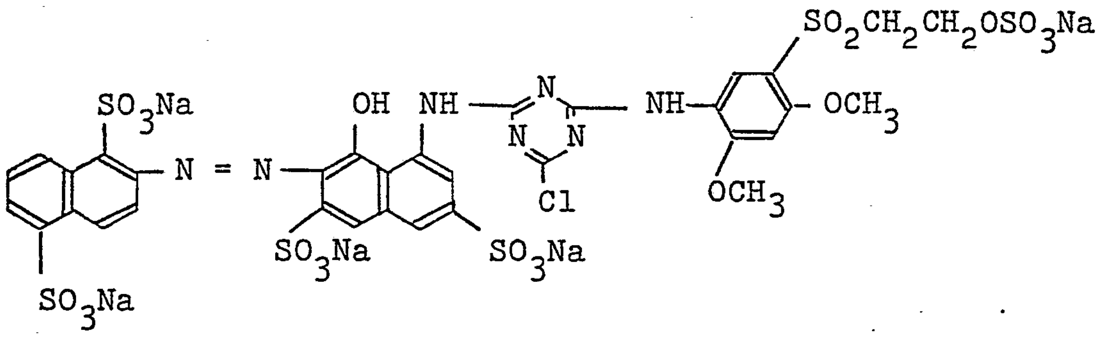
The thus prepared solution of diazonium salt was added to the foregoing reaction mixture, and the resulting mixture was stirred for 5 hours at 10°C or below while keeping the pH at 6.5 to 7.5 by the addition of a 15 % aqueous solution of sodium hydroxide. After raising the temperature of the mixture to 30°C, 4-amino-2,5-dimethoxyphenyl β-sulfatoethylsulfon (18.6 parts) was added thereto, and the mixture was stirred for 5 hours while keeping the pH at 5 or less. The reaction mixture was salted out by the addition of sodium chloride (150 parts), and the precipitated product was separated by filtration, washed and dried to obtain 57 parts of a dye having the following formula.



(λ_{max} = 540 nm)

Example 3

Into an iced aqueous solution containing cyanuric chloride (18.5 parts) was added an aqueous solution of tetrasodium 5-amino-4-hydroxy-3-(1,5-disulfo-2-naphthylazo)-2,7-naphthalenedisulfonate (72.1 parts) which had been produced in a conventional manner using 5-amino-4-hydroxy-2,7-naphthalenedisulfonic acid as a coupling component and 2-amino-1,5-naphthalenedisulfonic acid as a diazo component, and the mixture was stirred for 7 hours under cooling while keeping the pH at 5 or less by the addition of a 15 % aqueous solution of sodium hydroxide. After raising the temperature of the mixture to 20°C, 5-amino-2,4-dimethoxyphenyl β-sulfatoethylsulfon (37 parts) was added thereto. The resulting mixture was heated to 30°C while keeping the pH at 5 or less by the addition of sodium carbonate, and stirred for 3 hours at the same temperature. The reaction mixture was salted out by the addition of sodium chloride (300 parts), and the precipitated product was separated by filtration, washed and then dried at 60°C to obtain 123 parts of a dye of the formula,



The above procedure was repeated, except that 3-aminophenyl vinylsulfon (20 parts) was used in place of 5-amino-2,4-dimethoxyphenyl β-sulfatoethylsulfon, whereupon 101 parts of a dye having a vinylsulfonyl group were obtained in place of the β-sulfatoethylsulfonyl group in the dye of Example 1.

Example 4

Into an iced aqueous solution containing cyanuric chloride (9.2 parts) was added 4-amino-2,5-dimethoxyphenyl β-sulfatoethylsulfon (17 parts), and the mixture was stirred for 5 hours under cooling while keeping the pH at 5 or less by the addition of a 20 % aqueous solution of sodium carbonate. After raising the temperature of the mixture to 30°C, a neutral solution containing 5-amino-4-hydroxy-2,7-naphthalenedisulfonic acid (15.9 parts) was added thereto, and the resulting mixture was stirred for 10 hours at the same temperature while keeping the pH at 6 or less. The reaction mixture was salted out by the addition of sodium chloride (75 parts) to obtain a precipitated product, which was then separated by filtration and washed. The whole of the product obtained was again dissolved and cooled to 10°C or below, and to this solution was added a diazonium salt solution obtained using 2-amino-1,5-naphthalenedisulfonic acid (12 parts) in the same manner as in Example 1. The mixture was stirred for 5 hours while keeping the pH at 6 to 7 by the addition of sodium carbonate. Thereafter, the reaction mixture as such was subjected to spray-drying, to give 43 parts of a dye having the same formula as of Example 2.

Example 5

Example 4 was repeated, except that 3-aminophenyl β-hydroxyethylsulfon (10.5 parts) was used in place of 4-amino-2,5-dimethoxyphenyl β-sulfatoethylsulfon. The resulting dye precursor (40 parts) was dissolved in sulfuric acid (400 parts) at 0°C, and the solution was poured into ice water at -5° to 0°C, then gradually neutralized at 5°C or less to pH 6 by the addition of a 10 % aqueous sodium hydroxide solution and sodium carbonate, and thereafter salted out at 30°C by the addition of sodium chloride (450 parts). The precipitated product was separated by filtration, washed and then dried at 60°C, thereby to obtain 35 parts of a dye having the same formula as of Example 1.

Example 6

The dye (0.3 part) obtained in Example 1 was dissolved in water (200 parts), and sodium sulfate (20 parts) and cotton (10 parts) were added to the dye liquor, which was then heated to 40°C. After 30 minutes had passed, sodium carbonate (4 parts) was added, and dyeing was carried out at the same temperature for 1 hour. After dyeing was finished, the dyed cotton was rinsed and soaped.

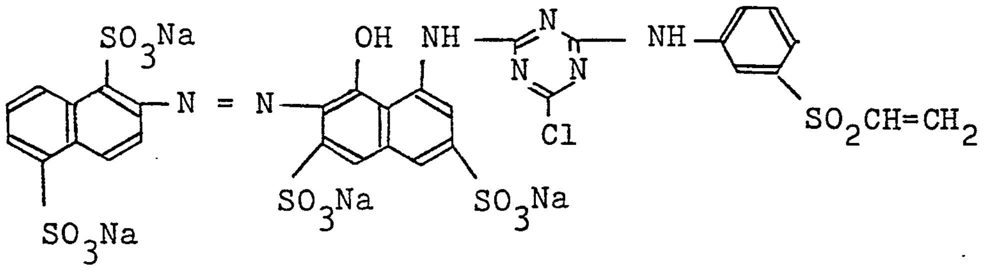
Thus, dyeings of brilliant red colors having excellent fastnesses to chlorine, light and perspiration-light were obtained.

Example 7

The dye (0.3 part) obtained in Example 2 was dissolved in water (200 parts), and sodium sulfate (20 parts) and cotton (10 parts) were added to the dye liquor, which was then heated to 50°C. After 20 minutes had passed, trisodium phosphate (3 parts) was added, and dyeing was carried out at the same temperature for 1 hour. After dyeing was finished, the dyed cotton was rinsed and soaped to obtain dyeings having excellent fastnesses to chlorine, light and perspiration-light.

Example 8

The dye (0.3 part) obtained in the last paragraph of Example 3, which contains as its main component a dye of the formula,



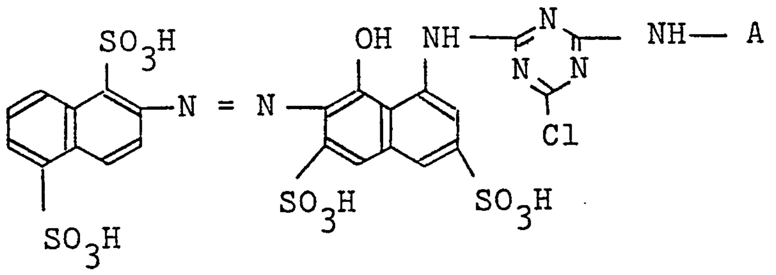
(λ_{max} = 540 nm)

was dissolved in water (200 parts), and sodium sulfate (20 parts) and cotton (10 parts) were added to the dye liquor, which was then heated to 70°C. After 20 minutes had passed, sodium carbonate (4 parts) was added, and dyeing was carried out at the same temperature for 1 hour.

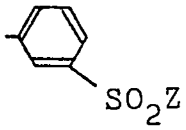
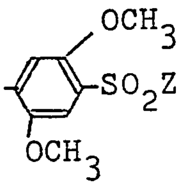
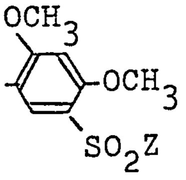
After dyeing was finished, the dyed cotton was rinsed and soaped to obtain dyeings of brilliant red colors having excellent chlorine fastness.

WHAT IS CLAIMED IS:

1. Reactive monoazo dyes of the general formula (I)

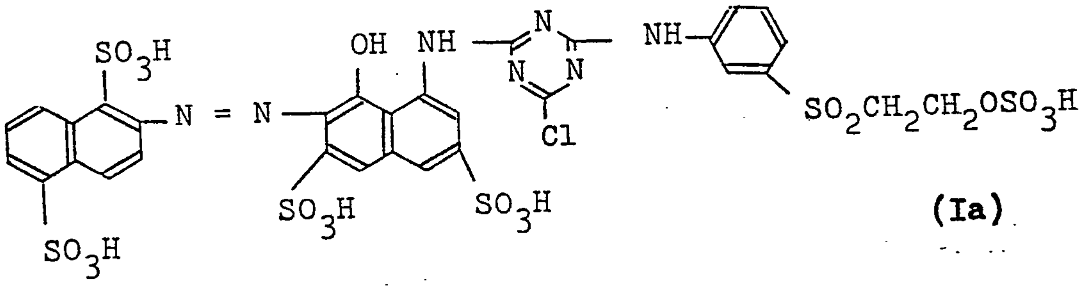


(I)

wherein A is  ,  or 

in which Z is $-CH_2CH_2OSO_3H$ or $-CH=CH_2$, and their salts, including alkali metal salts.

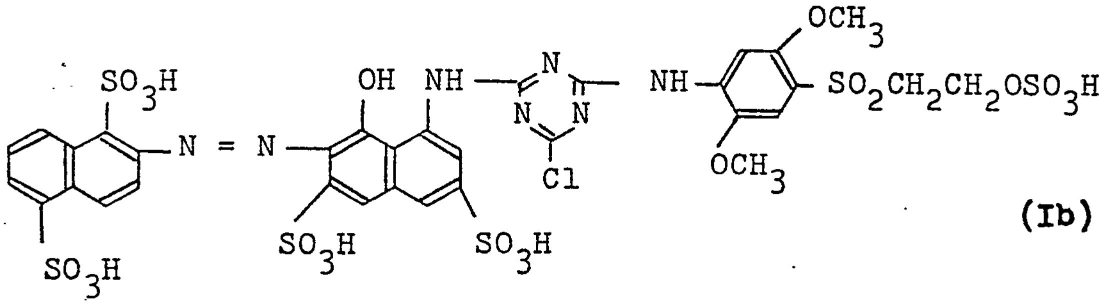
2. Reactive monoazo dyes of the formula (Ia)



(Ia)

and their salts, including alkali metal salts.

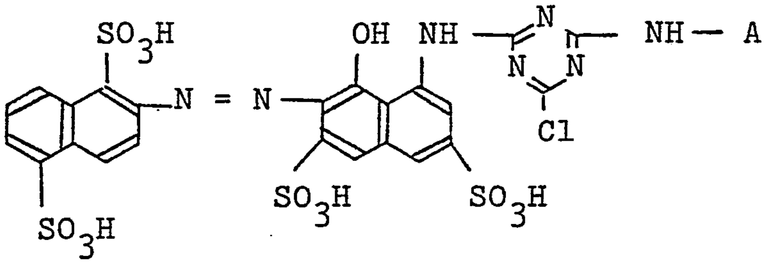
3. Reactive monoazo dyes of the formula (Ib)



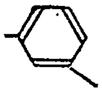
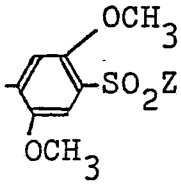
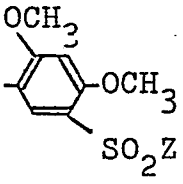
(Ib)

and their salts, including alkali metal salts.

4. A process for producing the reactive monoazo dyes of the general formula (I)



(I)

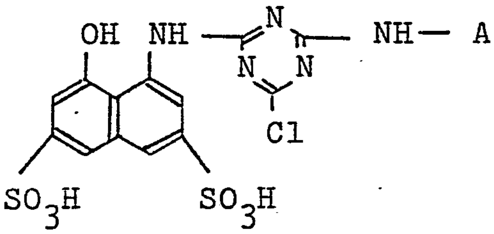
wherein A is  ,  or 

in which Z is $-CH_2CH_2OSO_3H$ or $-CH=CH_2$, which comprises

(i) reacting cyanuric chloride with 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid or an aniline compound of the formula (II)

$$A - NH_2 \qquad (II)$$

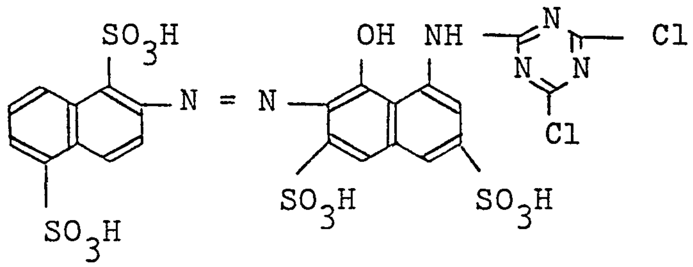
wherein A is as defined above, followed by reaction with the aniline compound (II) or 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid, respectively, to obtain a monochlorotriazinyl compound of the formula (III)



(III)

wherein A is as defined above, and reacting the monochlorotriazinyl compound (III) with diazotized 2-amino-1,5-naphthalenedisulfonic acid,

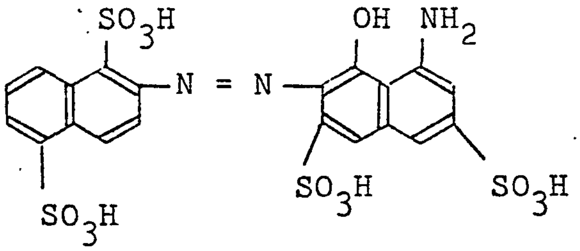
(ii) reacting 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid with cyanuric chloride and **thereafter** with diazotized 2-amino-1,5-naphthalenedisulfonic acid to obtain a dichlorotriazinyl compound of the formula (IV).



(IV)

and reacting the dichlorotriazinyl compound (IV) with the aniline compound of the formula (II),

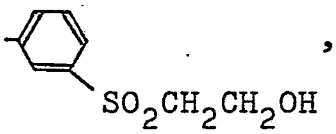
(iii) reacting 4-hydroxy-5-amino-2,7-naphthalenedisulfonic acid with a diazotized 2-amino-1,5-naphthalenedisulfonic acid under alkaline conditions to obtain a monoazo compound of the formula (V),

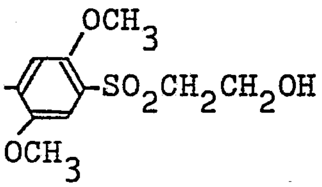


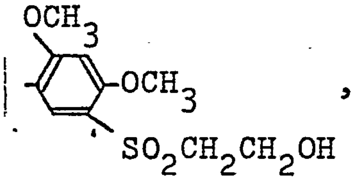
(V)

and reacting the monoazo compound (V) with cyanuric chloride and the aniline compound of the formula (II) in this order, or

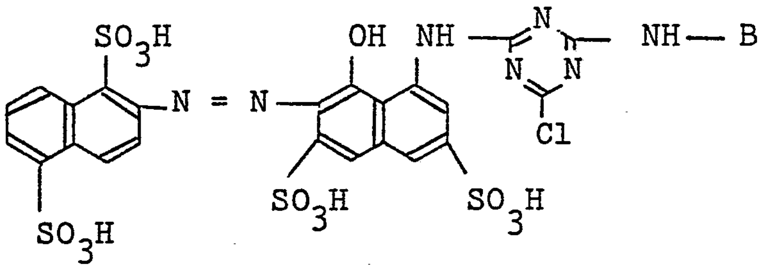
(iv) carrying out a reaction in a manner (i), (ii) or (iii) as defined above, except using an aniline compound of the formula (VI) in place of the aniline compound of the formula (II), the formula (VI) being

B-NH$_2$, wherein B is 

, 

or 

, and reacting the resulting compound of the formula (VII)



(VII)

wherein B is as defined above, with sulfuric acid to obtain the compound of the formula (I) having β-sulfatoethylsulfonyl group ($-SO_2CH_2CH_2OSO_3H$) as Z, and if necessary followed by elimination of sulfuric acid to obtain the compound of the formula (I) having vinyl group ($-CH=CH_2$) as Z, and if desired converting the compounds of the general formula (I) into their salts, including alkali metal salts.

5. Use of the compounds according to claims 1 to 3 for dyeing cellulosic fibers and cellulosic textiles.

European Patent
Office

EUROPEAN SEARCH REPORT

0022575

Application number

EP 80 10 4024

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	US - A - 3 223 470 (BOEDEKER, LANGBEIN, SOMMER, ZIMMERMANN, BERNER) The complete document *	1
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	CH - A - 410 237 (ICI) * Claim *	1
	--	
	FR - A - 2 084 024 (ICI) * Page 1, lines 1-28; page 10, lines 33-34 *	1

☒ The present search report has been drawn up for all claims

CLASSIFICATION OF THE APPLICATION (Int. Cl.3)

C 09 B 62/085
62/51
D 06 P 3/66

TECHNICAL FIELDS SEARCHED (Int. Cl.3)

C 09 B 62/085
62/08
62/04
62/028
62/026
62/022
62/02
62/006
62/002
62/51
62/507
62/503

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

Place of search	Date of completion of the search	Examiner
The Hague	24-09-1980	GINESTET

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